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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C09J 197/02, D21J 1/00

A1

(11) International Publication Number: WO 98/31763

(43) International Publication Date: 23 July 1998 (23.07.98)

(21) International Application Number: PCT/FI98/00025

(22) International Filing Date: 14 January 1998 (14.01.98)

(30) Priority Data:
970159 14 January 1997 (14.01.97) FI

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
In English translation (filed in Finnish).

(54) Title: LIGNIN-BASED ADHESIVES AND A PROCESS FOR THE PREPARATION THEREOF

(57) Abstract

The invention concerns a lignin and/or carbohydrate-based adhesive binder for fiber boards, particle boards and similar wood-based products, comprising a foamed mixture of an aqueous suspension of lignin and/or carbohydrates obtained from a process of pulping lignocellulosic materials, the mixture being foamed to 1.1 to 10 times the volume of the liquid mixture and the density of the foam being 0.1 to 0.9 kg/l, and the medium foam bubble diameter 0.01 to 0.05 mm. The invention also concerns a method of preparing lignin and/or carbohydrate-based adhesive binders for wood-based products, as well as particle boards, fiber boards or similar wood-based products comprising wood particles, flakes or fibres mixed with the adhesive binder. By foaming the adhesive, an even dispersion of the solids is provided, which improves the quality of the products and gives rise to substantial savings in adhesive use.

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Lignin-based adhesives and a process for the preparation thereof

The present invention relates to the preparation of particle boards, fiber boards, flake boards, plywood and similar wood-based products comprising lignocellulosic particles, fibers, flakes or veneer mixed and bonded together with an adhesive binder. In particular the present invention concerns novel lignin-based adhesives and a preparation process thereof as well as particle boards, fiber boards and flake boards manufactured by using the adhesives.

The rapid increase in the production of particle boards, flake boards and fiber boards, especially medium density fiber boards (in the following also abbreviated MDF boards), during the last decades has created a demand for adhesives that are inexpensive, available in large quantities, and independent of crude oil. Lignin meets well these requirements, and it does not contain any formaldehyde, which traditionally has been considered a serious problem with conventional urea-formaldehyde (UF) adhesives. As a major wood component, native lignin is neither hygroscopic nor soluble in water. However, during technical pulping lignin becomes soluble in water, due to degradation and chemical changes.

The use of spent sulphite liquor (SSL) as an adhesive for paper, wood and other ligno-cellulosic materials is well-known in the art, and a large number of patent applications has been filed during the last three decades for the use of lignin products as adhesives for particle board, plywood and fiber board instead of conventional PF or UF adhesives. Reference is made to DE Patents Nos. 3 037 992, 3 621 218, 3 933 279, 4 020 969, 4 204 793 and 4 306 439 and PCT Applications published under Nos. WO 93/25622, WO 94/01488, WO 95/23232 and WO 96/03546.

The main drawback of using SSL as an adhesive for fiber board manufacture is its hygroscopicity. For this reason it cannot really compete with other natural or synthetic adhesives. When SSL is applied as an adhesive, it has to be converted to an insoluble substance by curing. Chemically the curing of lignin is a cross-linking process, which leads to new carbon-carbon and ether bonds between different lignin molecules or within one macromolecule. Inter- as well as intramolecular cross-linking reactions decrease the

solubility and swelling of lignin. Cross-links in lignin can be achieved either by condensation or by radical coupling reactions. For the condensation reactions, either high temperatures and long heating times or mineral acids are required, which cause structural changes or charring in the wood particles. Recently, cross-linking of the lignosulphonate molecules by radical combinations has been developed. In most cases additional cross-linking agents for lignin are necessary, such as epoxides, polyisocyanates, polyols, poly(acryl amide)s, poly(ethylene imine) and aldehydes.

Further, it has been shown that laccase enzymes and other peroxidases can be used as polymerization or curing catalysts of lignin (DE Patent No. 3 037 992, WO 96/03546). However, the enzymes for creating radical reactions have shown limited success so far. Fibers and wood chips used in the production of the fiber board contain 5 - 20 % water and the laccases used need some water to effectively catalyze the polymerization reaction needed for extensive bonding of the fiberboard. Kraft lignin like native lignin to its major part is, however, insoluble in water and thus two solid phases are formed on the production line. An uneven distribution of the solids causes spotting and major failure in the strength properties of the board formed in the pressing stage.

For the above mentioned reasons, lignin-based board production processes have not, so far, led to any major practical applications.

The present invention aims at eliminating the problems relating to the prior art. In particular it is an object of the present invention to provide a novel lignin-based adhesive binder for use with particle boards, fiber boards and similar wood-based products. It is another object of the present invention to provide new particle boards, fiber boards and similar wood-based products. It is a third object to provide a method for manufacturing the adhesive binder.

These and other objects, together with the advantages thereof over known lignin-based adhesives and processes for the preparation thereof, which shall become apparent from the specification which follows, are accomplished by the invention as hereinafter described and claimed.

According to the invention, lignin, or lignin polymerized with oxidative enzymes, is added to and mixed with the fibers or chips or flakes used as lignocellulosic raw material of the wood-based product in the form of a foam to provide an even dispersion of the solids.

Foamed UF and PF adhesives are known in the art. Said foams are used for improving process performance and product quality especially in adhesives with high solid contents. CA Patent Application No. 2,114,258 describes particle board production by using foamed mixtures of UF resin and animal blood. Also DE 3,644,067 describes the use of foamed materials for binding of fibers and flakes to produce a homogeneous adhesive application of fine particles (fibers or powders) on the furnish. T. Sellers describes in Forest Prod. J. 38 (1988) p. 55-56 the superior performance of foamed UF and PF resins in particle board manufacture especially at higher solids content of the adhesive. However, none of the prior art references mentions foaming of lignin-containing adhesive binders. It should further be noticed that, in the solutions described above, the composition of the gas is not important.

The lignin-based adhesive binder composition according to the present invention comprises an aqueous suspension of lignin isolated from a process of pulping lignocellulosic raw materials. The suspension has been foamed to 1.05 to 10, preferably, 1.1 to 8, in particular to 1.2 to 5 times the volume of the liquid mixture. It is preferred to use polymerized kraft lignin as the lignin component. The foam will homogenize the solid phase and the liquid phase, increase the viscosity of the mixture and prevent sedimentation of the solids.

According to a preferred embodiment of the present invention, the oxygen required by the lignin adhesive binder is introduced into the adhesive binder in the form of an evenly divided, homogenous foam with small bubbles. The oxygen-containing foamed structure will also provide more oxygen for the oxygen-dependent oxidase catalyzed lignin polymerization. Because of its large volume, the foam will cover more homogeneously the wood fibres and wood particles during the preparation of the boards. This will lead to better strength values and better control of the use of the adhesive binder in the production of wood-based products.

The invention will now be explained in more detail with the aid of the following detailed description and with reference to a number of working examples.

Figure 1 shows the effect of oxygen supply to glueing efficiency of lignin-based adhesive binders in particle board glueing;
Figure 2 shows the bubble size distribution in foamed lignin-based adhesive binders without dispersing agents;
Figure 3 shows the bubble size distribution in foamed lignin-based adhesive binders containing 5 % of CMC;
Figure 4 shows the bubble size distribution in foamed lignin-based adhesive binders containing 5 % of wood extractive (a lignin/carbohydrate fraction called "anionic trash" obtained from the MDF process); and
Figure 5 shows the swellings of MDF boards, small scale tests.

Within the context of the present invention, the terms "adhesive", "adhesive binder" and "resin" designate a chemical composition which, in the wet stages of the manufacture of, e.g. particle and fiber boards, provides adhesion between the particles, fibers or flakes. After heat compression during board manufacture, the composition containing polymerized resin works as a binder which keeps the particles or fibers or flakes bonded together.

The term "wood-based product" denotes any lignocellulose-based products, such as particle boards, fiber boards (including high and medium density fiber boards, i.e. hard boards and MDF boards), flake boards, plywood and similar products constituted by particles, fibers or flakes of vegetable origin, in particular derived from wood or annular or perennial plants mixed with and bonded together with adhesive binders.

For polymerizing lignin and carbohydrates of soluble wood fractions, oxidative enzymes capable of catalyzing oxidation of phenolic groups can be used. These enzymes are oxidoreductases, such as peroxidases and oxidases. "Peroxidases" are enzymes which catalyze oxidative reaction using hydrogen peroxide as their substrate, whereas "oxidases" are enzymes which catalyze oxidative reactions using molecular oxygen as their substrate. Phenoloxidases (EC 1.10.3.2 benzenediol:oxygen oxidoreductase) catalyze the oxidation of

o- and p-substituted phenolic hydroxyl and amino/amine groups in monomeric and polymeric aromatic compounds. The oxidative reaction leads to the formation of phenoxy radicals and finally to the polymerization of lignin and possibly the carbohydrate matter. In the method of the present invention, the enzyme used may be any of the enzymes catalyzing the biological radical formation and secondary chemical polymerization of low molecular weight lignins, such as laccase, tyrosinase, peroxidase or oxidase.

As specific examples of oxidases the following can be mentioned: laccases (EC 1.10.3.2), catechol oxidases (EC 1.10.3.1), tyrosinases (EC 1.14.18.1) and bilirubin oxidases (EC 1.3.3.5). Laccases are particularly preferred oxidases. They can be obtained from bacteria and fungi belonging to, e.g., the following strains: *Aspergillus*, *Neurospora*, *Podospora*, *Botrytis*, *Lentinus*, *Polyporus*, *Rhizoctonia*, *Coprinus*, *Coriolus*, *Phlebia*, *Pleurotus*, *Fusarium* and *Trametes*.

Suitable peroxidases can be obtained from plants or fungi or bacteria. Preferred peroxidases are those which originate from plants, in particular horseradish peroxidase and soy bean peroxidase.

The terms "surfactant" or "surface active agent" are synonymously used to designate compounds which have affinity to water and to hydrophobic (e.g. fatty) materials and decrease surface tension, thus aiding the hydrophobic materials to suspend in water and providing a sufficient stability for the suspension and the foam.

Adhesive component

As mentioned above, lignin of different origins can be used as the adhesive component of the present foamed adhesive binders. In particular, isolated lignin of, e.g., the sulphate, sulphite, ORGANOSOLV and MILOX processes can be used.

However, in addition to lignin or instead of it, various soluble wood fractions can also be employed. Thus, it is known in the art that during mechanical refining of chips, a part of the compounds of the fibrous raw material is dissolved (about 1 % of the fiber weight). This

fraction contains primarily the same chemical components as the fibers (carbohydrates, extractives and lignin). To mention an example: the soluble fraction of softwood chips contains some 40 to 70 % carbohydrates, 10 to 25 % lignin and 1 to 10 % extractives, whereas hardwood pulping process water contains some 20 to 60 % carbohydrates, 10 to 25 % lignin and 10 to 40 % extractives.

It has been found that this soluble lignin/carbohydrate fraction obtainable from mechanical or chemimechanical pulping is particularly useful as an additive or adjuvant for gluing of particles boards, fiber boards and other similar wood-based composite products. Particularly good gluing is achieved if this fraction (as is the case with lignin) is polymerized with laccase (or similar) oxidase enzyme(s). The results are on the same level or even better as those obtainable with conventional phenol or urea formaldehyde resins.

It should be noticed that a similar soluble fraction can be obtained by treating lignocellulosic raw material, such as wood fibers or saw dust, with hydrolases, e.g. cellulases, hemicellulases and pectinases.

Manufacture of the foamed adhesive binder

According to the present invention, a lignin and/or carbohydrate-based adhesive is produced by dispersing lignin and/or carbohydrate matter into water to form a suspension and bubbling a gas through the suspension such that bubbles having a medium diameter of 0.001 to 1 mm, in particular about 0.01 to 0.1 mm, are formed.

The foam is produced by the use of a surface active agent that can be anionic, cationic or non-ionic. Thus, the surfactant can be selected from the group consisting of alkylsulfonate or alkyl benzene sulfonate, Tween® and other commercial compounds, fatty acid soaps, lignosulfonates, sarcosinates, fatty acid amines or amines or poly(oxyetylene alcohol)s and wood and plant extractives. Foam stabilizers and solid surfactants, such as CMC, gelatin, pectin, wood extractive and similar compounds, can be used to produce and enhance the foam stability. A small amount of the surface active compounds is needed, i.e. about 0.01 to 10 %, in particular about 0.05 to 5 %.

The foam can be produced by foaming in a static foamer or in a turbulent foam cell by using known mixing technology. It is preferred to use oxygen-containing gases. such as air, oxygen enriched air, oxygen or pressurized systems of these. The importance of using oxygen-containing gases is discussed in further detail below.

The foam produced is essentially stable during handling, storage, transport and manufacture of wood-based products and it has a density in the range of 0.1 to 0.9 kg/l, in particular about 0.2 to 0.7 kg/l, and a medium bubble diameter in the range of 0.005 to 0.1 mm, in particular about 0.01 to 0.1 mm, preferably about 0.02 mm. The foam can be produced separately from the fibers and chips, which are mixed with the foam by extruding or spraying the foam to the fibers or chips. The foam can also be produced simultaneously by mixing the fibers or chips with the foam chemicals. the lignin and the enzyme (e.g. the laccase).

The method according to the present invention can be used for all oxidase-catalyzed, previously unsuccessfully suggested enzyme-catalyzed glueing processes using oxidases. The enzyme used can be any of the enzymes catalyzing the oxidation and polymerization of aromatic compounds or lignins, such as laccase, tyrosinase, or other oxidases, as mentioned above. The amount of enzyme used varies depending on the activity of the enzyme and on the amount of dry matter content of the composition. Generally, the oxidases are used in amounts of 0.001 to 10 mg protein/g of dry matter, preferably about 0,1 to 5 mg protein/g of dry matter. The activity of the oxidase is about.1 to 100,000 nkat/g, preferably over 100 nkat/g.

In connection with the present invention it has been found that oxygen plays a decisive role in the enzymatic polymerization of lignin of any origin. The same applies to water-soluble wood fractions containing carbohydrates, lignin and extractives. This is important in particular for the production of adhesives for the manufacture of fiber boards, particle boards and flake boards and other similar wood-based products. Thus, in addition to the reactant of the lignin/carbohydrate material, also oxygen is needed in sufficient amounts. The oxidative reaction leads to the formation of phenoxy radicals and finally to the polymerization of lignin and other components of the material.

In the known methods discussed above. crosslinking was only partially achieved because of apparent limitations on the availability of oxygen. The limitation of the reaction by oxygen manifests itself in the long reaction times used, and in the poor strength properties obtained, thus impairing the result of the enzyme aided polymerization.

Oxygen can be supplied by various means, such as efficient mixing, air enriched with oxygen or by introducing oxygen by enzymatic or chemical means to the solution. However, according to the present invention, by foaming the suspension with an oxygen-containing gas it is possible to provide the oxygen needed for full lignin polymerization that continues with the fiber bound lignin due to the oxygen trapped in the foam and the dissolved enzyme. At the same time, the foamed structure gives enough strength to the adhesive binder so as to prevent sedimentation of water-insoluble lignin or the polymerized lignin and carbohydrates from the adhesive binder. thus producing failure in the production and in the fiber board product.

The present invention provides considerable advantages. Thus the present method provides a good viscose suspending medium to form an even dispersion of the solids, which improves substantially the quality of the board formed. The use of the foamed adhesives as described in this invention leads also to better control of the applications and to substantial savings in adhesive use.

By means of the invention it is possible to manufacture particle boards, fiber boards or similar wood-based products comprising particles, flakes or fibres by mixing particles. flakes or fibers mixed with a foamed lignin/carbohydrate-based adhesive binder as described above so as to incorporate 2 - 20 % of the solids of the adhesive binder into the wood-based product. It is possible to add any known adjuvants to the boards and products according to the invention. Thus, as shown in the examples below, wax (including wax dispersions) and similar substances can be incorporated in amounts of 0.01 to 5 %, in particular about 0.1 to 2 % (calculated from the weight of the wood substance).

Because of the foaming of the binder it will become evenly distributed throughout the wood-based product. about 0.04 to 0.08 g/cm^3 in any randomly selected volume unit of the

product. The internal bonding (IB) of a particle board according to the present invention is typically greater than 0.9 MPa, and the tensile strength of a fiber board according to the invention typically greater than 38 MPa.

The following non-limiting working examples illustrate the invention.

Example 1

Preparation of foamed kraft lignin-based adhesives and manufacture of fiber and particle boards

A. Small scale tests

Kraft lignin, Indulin AT, was used as a binder in MDF and particle board test panel glueing.

4.0 g of the lignin fraction was foamed to 1.5 times the original volume with an aeration loop for 30 min with 4.0 g of laccase concentrate (activity 4,000 nkat/g) in 2.0 g of 2 M sodium acetate buffer (pH 4.5). In case of MDF panels, 5.5 g of the mixture was then sprayed onto or mechanically mixed with 20 g of dry fibers and in case of particle board panels, 1.4 g of the mixture was either sprayed onto or mechanically mixed with 4.4 g of particle board chips. The fibers or chips had already been treated with 1 % of wax (Mobilex 54, 60 % emulsion) of the dry weight of the fibers. The reference tests were performed without laccase (water was used instead) and using commercial UF resins.

For strength tests, particle board panels of the size of 50 mm x 50 mm x 2 mm (weight about 5 g) were prepared by pressing for 2 min at a pressure of 30 kp/cm^2 and a temperature of 190 °C. MDF panels of the size of 90 mm x 90 mm x 2 mm (weight about 22 g) were prepared by pressing for 2 min at a pressure of 50 kp/cm^2 and a temperature of 190 °C. After pressing, the panels were then cut into four pieces (50 mm x 12 mm x 2 mm). These pieces were tested for parallel tensile strength with Zwick tensile strength testing equipment. The results are presented in Table 1.

B. Medium scale tests

The components of the adhesive binder; 192 g Indulin AT kraft lignin, 192 ml laccase culture concentrate (activity 4,000 nkat/ml) and 96 g 2M sodium acetate buffer of pH 4.5 were first mixed and then foamed with air to 1.3 times the original volume. Foaming was performed with an aeration loop which was inserted at the bottom of the mixing container during 30 min and at a temperature of 40 °C. The foamed mixture was then sprayed into a mixing drum. 1 % (wax d.w./wood d.w.) of hydrophobic wax dispersion (Mobilcer 60, 60 % dry matter) was also added to chips or fibers. Mixing time in the mixing drum was 30 min. 300 mm x 300 mm x 12 mm panels were pressed at a pressure of 30 kp/cm^2 and at a temperature of 190 °C. The pressing time was 60 s/mm. Neste Resins UF resins UREX 3620 or Fiburex were used as commercial references. Thickness, density, moisture content, internal bonding (vertical tensile strength) and swelling of the panels were determined. The results are shown in Table 2 and beneath.

Table 1. Small scale glueing tests, particle boards; tensile strengths

Foamed binder	Tensile strength MPa
Water	3 .0 ± 0.5
Indulin AT	7.2 ± 0.5
Indulin AT (90 %) + laccase	12.7 ± 0.6
Reference UF resin	12.5 ± 0.7

Table 2. Results of particle board glueing medium scale tests

Lignin used	Laccase activity nkat/g wood	Moisture content %	Thickness mm	Density kg/m^3	IB (Internal bonding) MPa
Indulin AT	330	2.9	11.8	760	0.95±0.06
UREX 3620		9.5	11.7	795	1.0±0.05

Swelling of the best particle board test panels glued with the foamed lignin-based in a 2 h swelling test was only 7.4 % and in a 24 h swelling test 20.5 %.

When the resin was prepared with no foaming, IB values were 0.2 - 0.3 MPa and the results of 24 hours swelling test over 100 %.

Example 2

Glueing of MDF boards with foamed kraft lignin-based adhesive binders

MDF fibers were glued according to the procedures presented in example 1. Results are shown in Tables 3 and 4.

Table 3. Small scale glueing tests, MDF boards, parallel tensile strengths

Foamed binder	Tensile strength MPa
Water	15.0 ± 2
Indulin AT	27.8 ± 2
Indulin AT (90 %) + laccase	39.0 ± 2
Reference UF resin	38.9 ± 5

Table 4. Results of MDF board glueing in medium scale tests

Lignin used	Laccase activity nkat/g wood	Moisture content %	Thickness mm	Density kg/m³	IB (Internal bonding) MPa
Indulin AT	270	2.9	10.8	813	0.52±0.06
UREX 3620		9.5	10.7	795	0.70±0.05

Swelling of the best MDF test panels glued with the foamed lignin-based in a 2 h swelling test was only 3.6 % and in a 24 h swelling test 6.4 %.

Example 3

Preparation of unfoamed adhesive binder of the laccase polymerized lignin and preparation of particle board from this binder

Unfoamed adhesives were prepared by repeating the procedure of Example 1 with the exception that no foaming was performed. The results are indicated in Table 5.

Table 5. Results of particle board glueing medium scale tests

Lignin used	Laccase activity nkat/g wood	Moisture content %	Thickness mm	Density kg/m³	IB (Internal bonding) MPa
Indulin AT	0	3.2	11.2	830	0.24±0.06
Indulin AT	330	2.9	11.8	760	0.31±0.06
UREX 3620		9.5	117	795	1.0±0.05

Swelling of the panels glued with the unfoamed lignin-based in a 2 h swelling test was 25 % and in a 24 h swelling test over 100 %.

Example 4

Preparation of unfoamed and foamed adhesives of kraft lignin (Indulin AT)

Small scale particle board test panels were manufactured according to the procedure of Example 1, but the foaming times of the foamed adhesive varied from 1 to 30 min.

The results are indicated in Figure 1, which shows the effect of oxygen supply on the glueing efficiency of lignin-based adhesive binders in particle board glueing. As apparent from the figure, the tensile strength of a board containing foamed binder is 35 to 40 % greater than the corresponding strength of a reference board.

Example 5

Bubble size distribution of foamed adhesive binders

When lignin-based binders are foamed according to the procedure presented in example 1, a typical volume growth of the binder is about 25 %, varying from 10 to 80 %. Mean bubble

size is 85 μm varying from 30 to 500 μm.

Figure 2 shows the bubble size distribution in foamed lignin-based adhesive without dispersing agents. Figure 3 shows the bubble size distribution in foamed lignin-based adhesive containing 5 % of CMC, and Figure 4 shows the bubble size distribution in foamed lignin-based adhesive containing 5 % of wood extractive ("anionic trash" from the MDF process).

Depending on the dispersing or foaming agent or foamer used, the volume growth and the bubble size of the foamed adhesive can be adjusted. With 5 % addition of CMC, volume growth in foamed lignin-based adhesive prepared according to the procedure presented in Example 1, was 50 %, mean bubble size being 50 μm, ranging from 20 to 300 μm. Correspondingly, when a wood extractive, such as lyofilized anionic trash from the MDF process, was used as the foaming agent, there was a smaller (10 - 30 %) increase in the volume of the foamed adhesive. Mean bubble size was 20 μm, varying in the range of 10 to 30 μm.

Example 6

Swelling of MDF boards, small scale

The annexed Figure 5 shows the swelling results (24 h) of MDF boards in small scale tests (the relative swellings of boards manufactured in small size are greater than the swellings of standard boards), showing the effect of foamed adhesive on the relative swelling result as well as the effect of the surfactant used as an adjuvant in the foamed adhesive on the same result. The effect of the surfactant on the foam composition has been shown in Figures 2 and 3.

WHAT IS CLAIMED IS:

1. A lignin and/or carbohydrate -based adhesive binder for fiber boards, particle boards and similar wood-based products, comprising a foamed mixture of an aqueous suspension of lignin and/or carbohydrates obtained from a process of pulping lignocellulosic materials, the mixture being foamed to 1.1 to 10 times the volume of the liquid mixture and containing oxidative enzymes capable of catalyzing oxidation of phenolic groups.

2. The adhesive binder according to claim 1, wherein the lignin comprises polymerized kraft lignin.

3. The adhesive binder according to claim 1, wherein the carbohydrate matter comprises a soluble fraction obtainable from mechanical or chemimechanical pulping of lignocellulosic raw material.

4. The adhesive binder according to claim 1, wherein the foam has a solids content of 1 - 90, preferably about 5 - 60 % by weight.

5. The adhesive binder according to claim 1, wherein the density of the foam is in the range from 0.1 to 0.9 kg/l, in particular about 0.2 to 0.7 kg/l, and the medium foam bubble diameter is in the range of 0.005 to 0.1 mm, in particular about 0.01 to 0.05 mm, preferably about 0.02 mm.

6. The adhesive binder according to claim 1, wherein the foam contains surfactants in an amount of 0.1 to 10, preferably 0.2 to 5 % by weight of the aqueous suspension.

7. The adhesive binder according to claim 6, wherein the surfactants are selected from the group consisting of liquid and solid surfactants.

8. The adhesive binder according to claim 7, wherein the surfactants are selected from the group consisting of anionic, cationic or non-ionic agents.

9. The adhesive binder according to claim 7 or 8, wherein the surfactants are selected from the group consisting of alkylsulfonate, alkyl benzene sulfonate, polysorbates, fatty acid soaps, lignosulfonates, sarcosinates, fatty acid amines, poly(oxyetylene alcohol)s, carboxy methyl cellulose, gelatin, pectin, wood and plant extractives, and mixtures thereof.

10. The adhesive binder according to claim 7 or 8, wherein the surfactant comprises a wood extract, such as a hydrocarbon-based water soluble fraction obtained from refining of lignocellulosic raw material.

11. The adhesive binder according to claim 9, wherein the surfactant comprises a mixture containing 10 - 90 wt-% of the hydrocarbon-based water soluble fraction and 90 - 10 wt-% of a surfactant selected from the group consisting of alkylsulfonate, alkyl benzene sulfonate, polysorbates, fatty acid soaps, lignosulfonates, sarcosinates, fatty acid amines, poly(oxyetylene alcohol)s, carboxy methyl cellulose, gelatin, pectin, wood and plant extractives and mixtures thereof.

12. The adhesive binder according to any one of the preceding claims, wherein the composition contains 0.01 to 1 wt-% of an oxidase or a peroxidase.

13. A method of preparing lignin and/or carbohydrate -based adhesive binders for fiber boards, particle boards and similar wood-based products, comprising the steps of

- providing lignin and/or carbohydrates isolated from a pulping process of lignocellulosic raw materials,
- forming an aqueous suspension of the lignin and/or carbohydrates, and
- foaming the aqueous suspension together with an oxidative enzyme capable of catalyzing oxidation of phenolic groups in order to provide a foamed adhesive binder composition.

14. The method according to claim 13, which comprises the steps of

- forming an aqueous suspension containing 1 - 90 % by weight of solid matter and comprising lignin and/or carbohydrates and surfactants, and
- foaming the aqueous suspension with an oxygen-containing gas to 1.1 - 10 times the

volume of the suspension to provide a foam having a solids content of 5 - 60 % by weight.

15. The method according to claim 13 or 14, wherein the lignin comprises polymerized kraft lignin.

16. The method according to claim 13 or 14, wherein a soluble fraction obtainable from mechanical or chemimechanical pulping of lignocellulosic material is used as the carbohydrate matter.

17. The method according to claim 15 or 16, which comprises the step of forming an aqueous suspension containing lignin and/or carbohydrates, an oxidase and surfactants.

18. The method according to any one of the claims 13 to 17, wherein the foam is produced by aerating the suspension in a flotation tank.

19. The method according to claim 15, wherein the surfactant is selected from the group consisting of alkylsulfonate, alkyl benzene sulfonate, polysorbates, fatty acid soaps, lignosulfonates, sarcosinates, fatty acid amines, poly(oxyetylene alcohol)s, carboxy methyl cellulose, gelatin, pectin, a hydrocarbon-based water soluble fraction obtained from refining of lignocellulosic raw material, and mixtures thereof.

20. Particle board, fiber board or a similar wood-based product comprising wood particles, flakes or fibers mixed with a lignin and/or carbohydrate -based adhesive binder, the adhesive binder being evenly distributed throughout the wood-based product and the concentration of the binder being about 0.04 to 0.08 g/cm^3 in any randomly selected volume unit of the product.

21. The wood-based product according to claim 20, wherein the internal bonding of the particle board test pieces is greater than 0.9 MPa.

22. The wood-based product according to claim 20, wherein the lignin-based adhesive

binder comprises polymerized kraft lignin.

23. A method of manufacturing a particle board, fiber board or a similar wood-based product comprising the step of mixing wood particles, flakes or fibers mixed with a lignin and/or carbohydrate -based adhesive binder according to any one of the claims 1 to 12 so as to incorporate 2 - 20 % of the solids of the adhesive binder into the wood-based product.

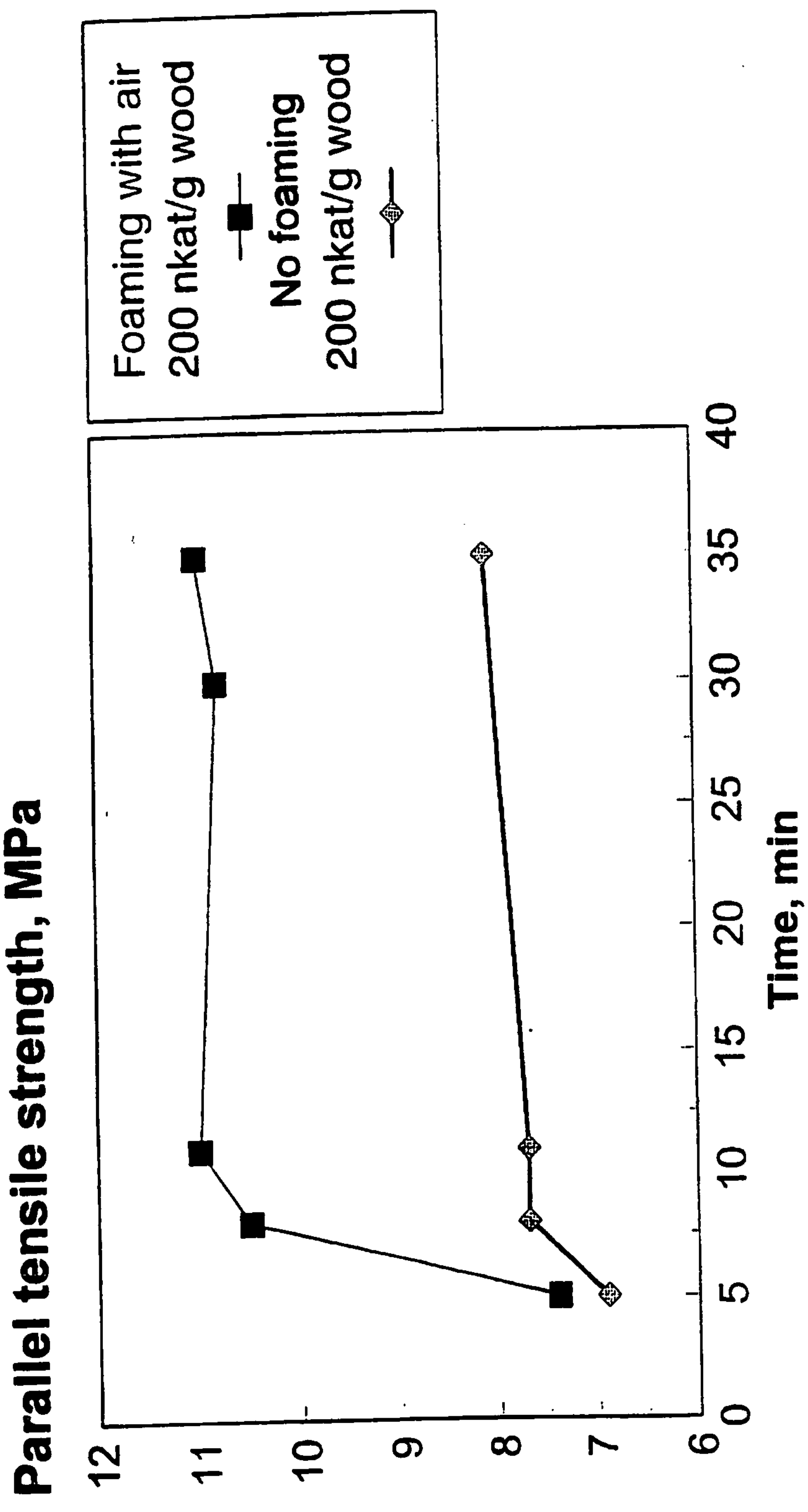
Parallel tensile strength, MPa
12
11
10
9
8
7
6
0
5
10
15
20
25
30
35
40
Time, min
Foaming with air
200 nkat/g wood
No foaming
200 nkat/g wood

FIG. 1

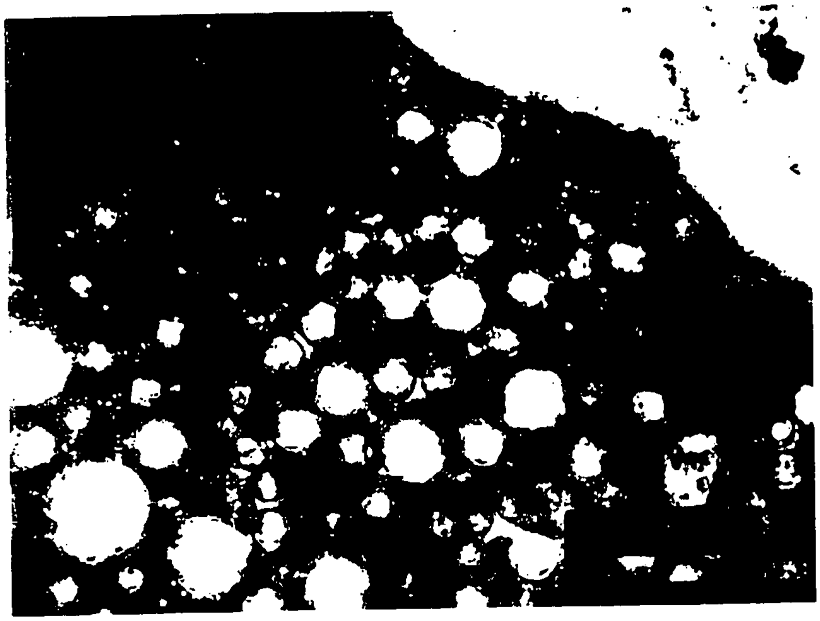

FIG. 2

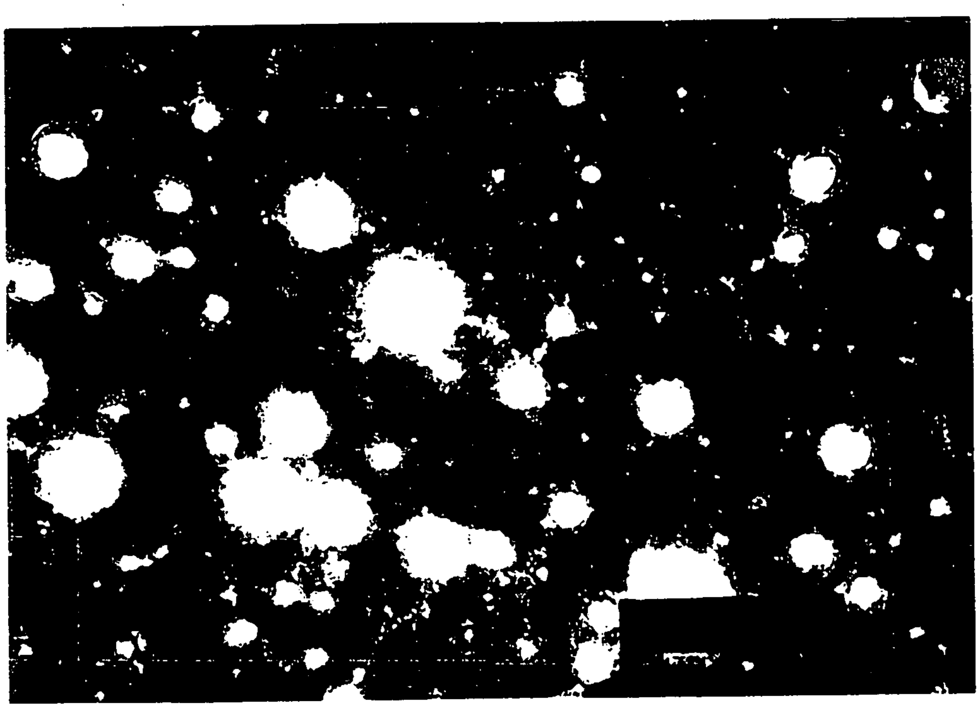

FIG. 3

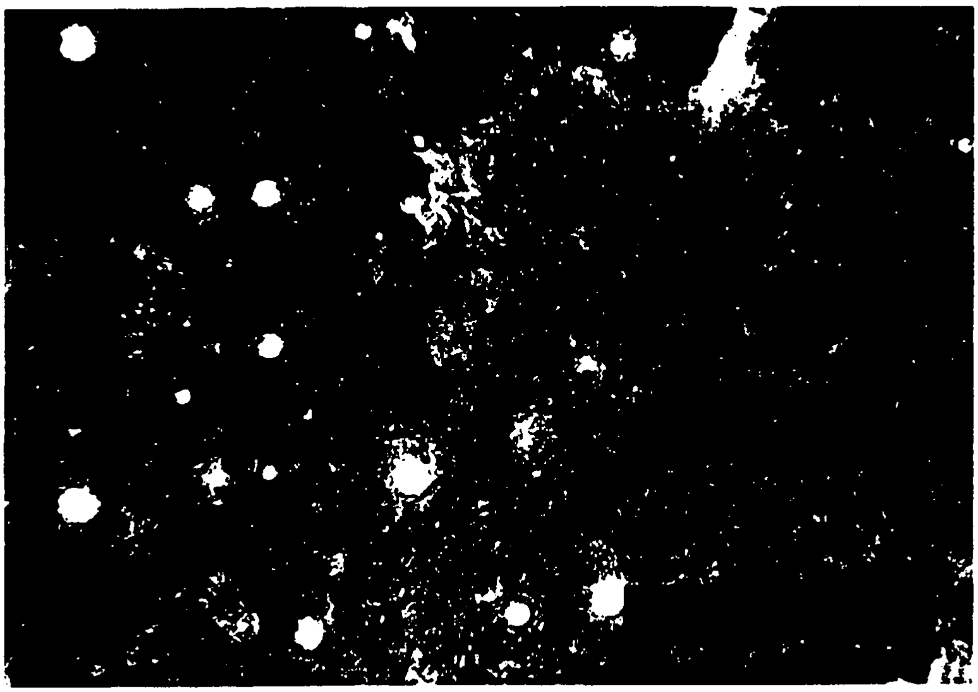

FIG. 4

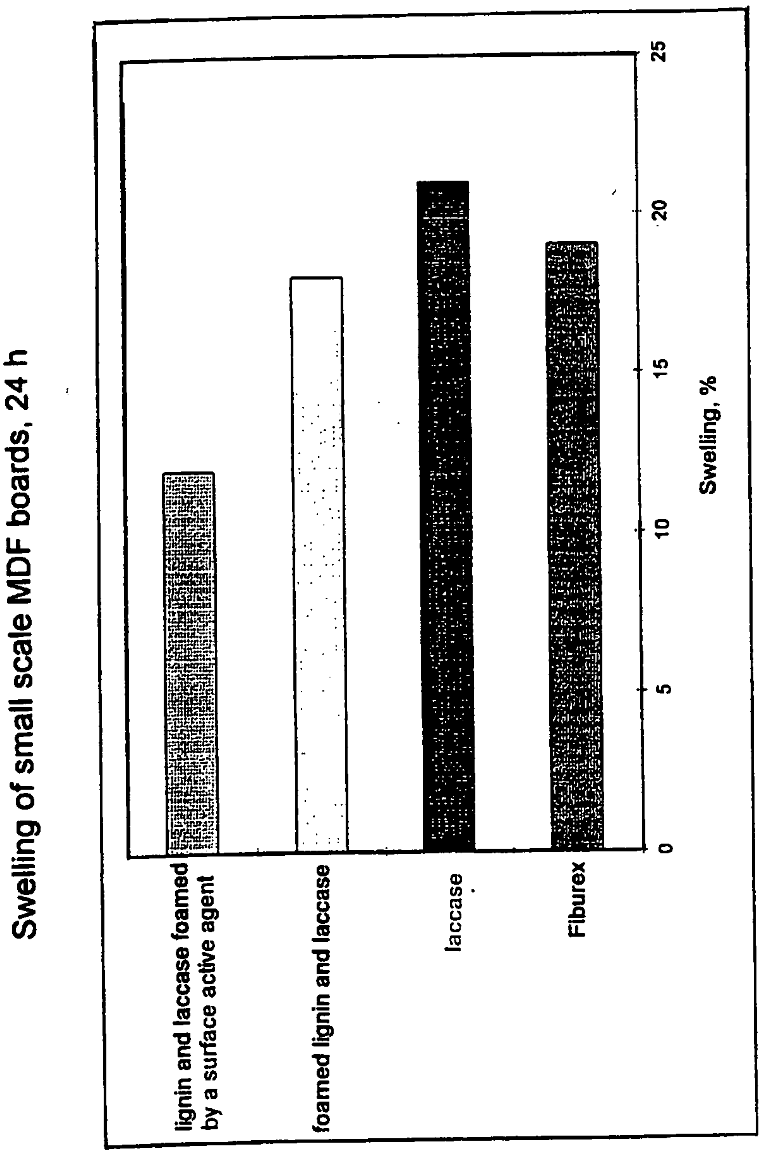
Swelling of small scale MDF boards, 24 h
lignin and laccase foamed by a surface active agent
foamed lignin and laccase
laccase
Fiburex
0
5
10
15
20
25
Swelling, %

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 98/00025

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09J 197/02, D21J 1/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09J, C08L, D21J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CAPLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9325622 A1 (NOVO NORDISK A/S), 23 December 1993 (23.12.93), page 1, line 15 - page 4, line 2, example 3, claims --	1-23
A	WO 9220857 A1 (CALL, HANS-PETER), 26 November 1992 (26.11.92), abstract, page 4, last paragraph - page 10, second paragraph; example 4; claims --	1-3
A	DE 3644067 A1 (KISS, GÜNTER H.), 30 June 1988 (30.06.88), abstract, claims --	1,18,20

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 May 1998	06 -05- 1998
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Sofia Nikolopoulou Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 98/00025

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 2848038 A1 (VVB FURHNIERE UND PLATTEN), 17 May 1979 (17.05.79), claim 1, page 3, paragraph 1 - paragraph 2 -- --------	1,6-7,18,20

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/04/98

International application No.

PCT/FI 98/00025

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9325622 A1	23/12/93	AU 4311493 A	04/01/94
WO 9220857 A1	26/11/92	AU 663501 B	12/10/95
		AU 1793392 A	30/12/92
		BR 9206013 A	15/11/94
		CA 2103260 A	18/11/92
		CN 1068161 A	20/01/93
		DE 4137761 A	19/11/92
		EP 0584176 A	02/03/94
		FI 935067 D	00/00/00
		JP 6508663 T	29/09/94
		NO 934148 A	04/01/94
DE 3644067 A1	30/06/88	NONE	
DE 2848038 A1	17/05/79	NONE	